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Oxidative Photocyclization of N^6 -Benzoyladenosine Derivatives.

Facile Formation of the Quinazolinopurine Ring System.

KAORU SHIMADA, MAGOICHI SAKO, KOSAKU HIROTA, YOSHIFUMI MAKI*

Irradiation of 2',3',5'-tri-*O*-acetyl- N^6 -benzoyladenosine derivatives (1) with UV-visible light in the presence of an oxidant such as pyrimido [5,4-*g*] pteridine *N*-oxide, tetracyanoethylene, *p*-dinitrobenzene, and iodine resulted in a novel type of the oxidative photocyclization leading to 8-(2',3',5'-tri-*O*-acetyl- β -*D*-ribofuranosylquinazolino [2,1-*i*] purin-12-one derivatives. The initial stage of the present reaction could be explained in terms of the C-*N* bond formation induced photochemically in the 1,3-diazahexatriene system which originates from the benzoylamidine moiety of 1. The present results provide a new method for the molecular manipulation of adenosines.

[Synthesis, 1987, 495]

Simple Synthesis of 5-(1-Alkenyl)uracil Derivatives by Palladium

Catalyzed Oxidative Coupling of Uracils with Olefines

KOSAKU HIROTA*, YOSHIKI ITOBE, YUKIO KITADE, YOSHIFUMI MAKI

A novel and convenient method for the C-C bond formation at the 5-position of uracil derivatives is described. An oxidative coupling of 1,3-dimethyluracil (1) with olefines in acetonitrile using an equivalent of palladium acetate resulted in the formation of 5-(1-alkenyl)uracil derivatives. This reaction was successfully applied to unprotected uridine leading to the corresponding 5-substituted uridines. In this reaction a stoichiometric amount of palladium acetate is required. When *t*-butyl perbenzoate was employed for the reoxidation of the produced palladium[Pd(O)], satisfactory results were obtained by the use of catalytic amount of palladium acetate.

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Palladium Catalyzed Coupling of 5-Hydroxyuracil Trifluoromethanesulfonates (Triflates) with Alkenes and Alkynes

KOSAKU HIROTA*, YUKIO KITADE, YOSHIKI ITOBE, YOSHIFUMI MAKI

Cross coupling of 5-hydroxyuracil triflates (1), which were prepared by treatment of 5-hydroxyuracils with trifluoromethanesulfonic anhydride, with electron deficient alkenes, e. g., methyl acrylate, methyl vinyl ketone, acrylonitrile, and styrene, in the presence of palladium chloride and triphenylphosphine in dimethylformamide afforded the corresponding 5-alkenyluracils in good yields. Analogous coupling reaction of (1) with alkynes gave 5-alkynyluracil derivatives. When the triflates (1) were treated with organocopper reagent [$R_2Cu(CN)Li_2$] without use of any catalyst, 5-alkyluracil derivatives were obtained.